Supporting Information: Aggregates of polar dyes: beyond the exciton model

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Ground state equilibrium coordinate

In the adiabatic approximation, the Hamiltonian for the single molecule is written neglecting the vibrational kinetic energy as follows:

$$\hat{H}(Q) = -\tau\hat{\sigma} + (2z_0 - g\sqrt{\frac{2\omega_v}{\hbar}}Q)\hat{\rho} + \frac{1}{2}\omega_v^2 Q^2 \tag{1}$$

The Hellmann-Feynman theorem allows to calculate the Q-derivative of the ground state energy as the expectation value of the $\hat{H}(Q)$ derivatives:

$$\frac{\delta E_g(Q,P)}{\delta Q} = -g\sqrt{\frac{2\omega_v}{\hbar}}\rho + \omega_v^2 Q \tag{2}$$

where $\langle g|\hat{\rho}|g\rangle = \rho$. The equilibrium coordinate $\bar{Q}$ is calculated imposing the vanishing of the energy derivative with respect to Q:

$$\bar{Q} = \sqrt{\frac{2\omega_v}{\hbar}} \frac{g}{\omega_v^2} \rho \tag{3}$$

Rotating the basis

Two new operators are defined as linear combinations of Pauli operators $\hat{\sigma}_{x,z}$, whose projections are defined by the parameter ρ:

$$\begin{aligned} \hat{S}_{x,i} &= -2\sqrt{\rho(1-\rho)}\hat{\sigma}_{z,i} + (1-2\rho)\hat{\sigma}_{x,i} \\ \hat{S}_{z,i} &= (1-2\rho)\hat{\sigma}_{z,i} + 2\sqrt{\rho(1-\rho)}\hat{\sigma}_{x,i} \end{aligned} \tag{4}$$

where i runs on the molecular sites. The above operators are then expressed in terms of creation and annihilation operators:

$$\begin{aligned} \hat{S}_{x,i} &= 1 - 2\hat{b}_i^\dagger \hat{b}_i \\ \hat{S}_{z,i} &= (\hat{b}_i^\dagger + \hat{b}_i) \end{aligned} \tag{5}$$

The operator $\hat{b}_i^\dagger$ creates an excitation on site i, by turning the molecule from state $|g\rangle$ to $|e\rangle$, while $\hat{b}_i$ destroys the excitation. These operators obey a Paulion algebra:

$$[\hat{b}_i, \hat{b}_j^\dagger] = \begin{cases} 1 - 2\hat{b}_j^\dagger \hat{b}_i, & \text{if } i = j \\ 0, & \text{if } i \neq j. \end{cases} \tag{6}$$

Applying the Lang-Firsov transformation to the vibrational states (see main text) and rotating the electronic basis as described above, the aggregate Hamitonian reads:

$$
\begin{aligned}
\mathcal{H} &= \sum_i \hat{n}_i \left[2(1-2\rho)(z_0 + M\rho - \varepsilon_v\rho) + 4\sqrt{\rho(1-\rho)}\tau\right] \\
&+ \sum_i (\hat{b}_i^\dagger + \hat{b}_i)\left[2\sqrt{\rho(1-\rho)}(z_0 + M\rho - \varepsilon_v\rho) - (1-2\rho)\tau\right] + \hbar\omega_v \sum_i \left(\hat{\tilde{a}}_i^\dagger \hat{\tilde{a}}_i + \frac{1}{2}\right) \\
&- g\left[(1-2\rho)\sum_i \hat{n}_i(\hat{\tilde{a}}_i^\dagger + \hat{\tilde{a}}_i) + \sqrt{\rho(1-\rho)}\sum_i (\hat{b}_i^\dagger + \hat{b}_i)(\hat{\tilde{a}}_i^\dagger + \hat{\tilde{a}}_i)\right] \\
&+ \sum_{i>j} V_{ij}\rho(1-\rho)\left[(\hat{b}_i^\dagger \hat{b}_j + \hat{b}_j^\dagger \hat{b}_i) + (\hat{b}_i^\dagger \hat{b}_j^\dagger + \hat{b}_j \hat{b}_i)\right] \\
&+ (1-2\rho)^2 \sum_{i>j} V_{ij}\hat{n}_i\hat{n}_j + 2\sqrt{\rho(1-\rho)}(1-2\rho)\sum_{i>j}\hat{n}_i(\hat{b}_j^\dagger + \hat{b}_j)
\end{aligned}
\tag{7}
$$

We impose the vanishing of the second term in Eq. 7 as follows:

$$
2\sqrt{\rho(1-\rho)}z(\rho) - (1-2\rho)\tau = 0 \quad \rightarrow \quad z(\rho) = \frac{1-2\rho}{2\sqrt{\rho(1-\rho)}}\tau \tag{8}
$$

Finally we rewrite the term in the square parenthesis in the first line of Eq. 7 as follows:

$$
2(1-2\rho)z(\rho) + 4\sqrt{\rho(1-\rho)}\tau = \frac{\tau}{\sqrt{\rho(1-\rho)}} \tag{9}
$$

Recalling Eq.10 (main text) we finally obtain the Hamiltonian in Eq. 6 (main text).

Convergence in medium and strong coupling

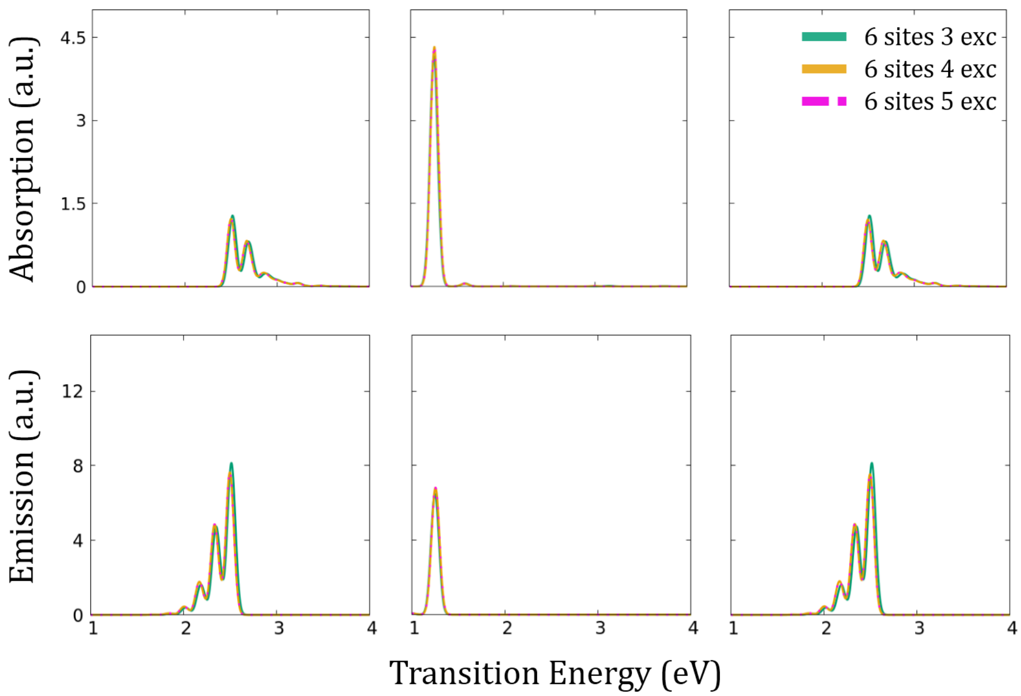

Figure S1: The same results as in Fig. 6, main text ($N = 6$), accounting for different value of N_e.

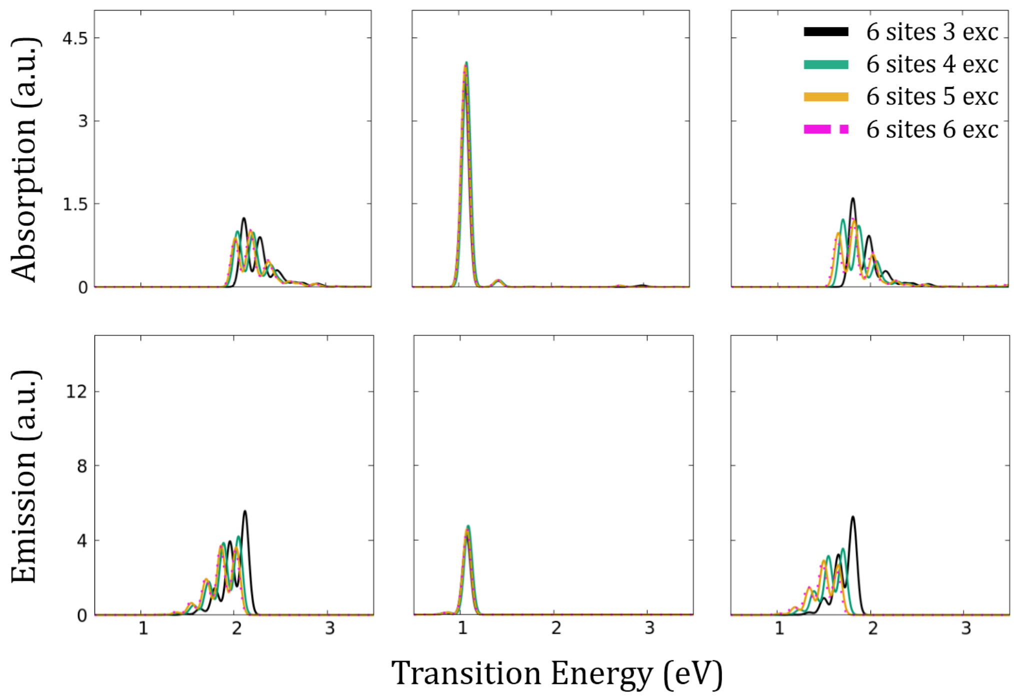

Figure S2: The same results as in Fig. 7, main text ($N = 6$), accounting for different value of N_e.